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QUALITY ASSURANCE FOR THE ACID PRECIPITATION MEASUREMENT PROGRAM IN THE UNITED STATES

by

P. L. Finkelstein*
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

*On assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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QUALITY ASSURANCE FOR THE ACID PRECIPITATION MEASUREMENT PROGRAM IN THE UNITED STATES

P.L. Finkelstein*
Environmental Protection Agency, Research Triangle Park, North Carolina 27711, USA

ABSTRACT

The U.S. National Atmospheric Deposition Program (NADP) is a confederation of scientists universities, and government agencies formed with the common interest of measuring acid rain in the United States. In order to insure that the data developed under this program are reliable, a quality assurance program was developed. This report reviews the major aspects of the NADP Quality Assurance Plan, including field operations, laboratory activities, and data handling.

INTRODUCTION

In the United States, the principal network for monitoring acid precipitation is operated by the National Atmospheric Deposition Program (NADP). NADP began in 1977 with two primary objectives: (1) to establish a deposition monitoring research network and (2) to establish an acid deposition effects research program. The deposition monitoring research program has as its goal the characterization of the significant geographical and temporal trends in the chemical components of precipitation of the United States. The NADP has a unique structure and mode of operation in that it represents the voluntary cooperation of hundreds of interested individuals and institutions. They operate the deposition monitoring sites and contribute financially to the support of the network management and laboratory. The independent sites (approximately 170 at this time) use standardized instrumentation and procedures to collect weekly wet deposition samples. The samples are sent to a Central Analytical Laboratory (CAL) operated by the Illinois State Water Survey. Measurements from the network are reviewed by the NADP Coordinator's Office, combined with information on network activities, placed in the NADP archive, and distributed as written reports. The data are also placed in the Environmental Protection Agency sponsored Acid Deposition Data System (ADS) where they are made available to the public.

Because of the need for the highest quality data and the rather diverse and non-centralized nature of the network, quality assurance is stressed in all aspects of the NADP. This includes stringent siting criteria and quality control on site activities, a rigorous quality assurance program at the CAL, and a quality assurance program on all aspects of the data management and reporting activity. The quality assurance activities and policy of NADP are specified in the NADP Quality Assurance Plan (NADP, 1984) which was developed by the NADP Quality Assurance Steering Committee, a group composed of the chairmen of all NADP technical subcommittees and other interested experts. This report reviews and summarizes the major features of the NADP Quality Assurance Plan for the sites, the CAL, and the data management and reporting activities of NADP.

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FIELD SITES

Wet deposition samples are collected once a week at each field site in an automated wet/dry collector. When a weekly sample is removed from the collector, it is weighed, its pH and conductivity are measured from an aliquot, and it is sent to the CAL for further analysis. Each site is located by the site sponsor following guidance in the NADP Site Selection and Certification Manual. Candidate sites are screened for suitability by the Coordinator's Office. A complete site description is kept on each site. A certification program which will reivew each site's suitability is being planned.

All routine operations, calibration, and required record and data handling procedures are given in a Site Operations Manual. To assist in maintaining good operations, several quality control procedures have been instituted at the field sites, including the use of check samples, control charts, site visits, and operator training. Check samples are supplied by the CAL to the sites for the pH and conductivity meters. Control charts on various instrument functions are kept on site and at the quality assurance coordinator's office. Regularly scheduled site visits by the site supervisor are to be made at least every six months, with standardized reports sent to the Quality Assurance Coordinator's Office. All new operators must take an operator's training course. In addition a refresher course is being developed for experienced operators. To better maintain the sites, regular maintenance is scheduled with records of all activities kept. Certain spare parts, such as pH electrodes, are bought in bulk by the CAL and distributed to the field sites on a regular basis.

External systems and performance audits are scheduled by the Quality Assurance Coordinator's Office. A new site is visited by an inspection team before it is started, and again at least once every three years. All measurements at the site are challenged during the audit, and a complete record of site activity is made. Any corrective action that is noted as a result of the audit is reported to the coordinator as well as at the site, so that follow-up on the problem is assured.

Accuracy of the sample measurements is determined from the site audits. Precision will be determined by having duplicate sampling at aproximately 10% of the sampling sites.

LABORATORY

The Central Analytical Laboratory (CAL), where all NADP deposition samples are analyzed, is operated by the Illinois State Water Survey. The laboratory performs analysis of wet deposition samples for the major ions, chloride, nitrate, phosphate, sulfate, calcium, magnesium, sodium, potassium, and ammonium; as well as for hydrogen (pH) and specific conductance.

Within the laboratory, quality assurance is a multitiered program which includes bench level quality control, laboratory management-level quality assurance, and external quality assurance monitoring. The overall goal of the laboratory program is to produce analytical data whose precision and accuracy are reliably quantified. The analytical goals are to achieve stated detection limits within acceptable tolerance levels.

Instrument calibration and standards preparation are among the most critical areas of laboratory quality control. Internal standards are produced, depending upon the ion, using

at least two of the following four procedures: (1) arrange for independent laboratory confirmation of the standard, (2) obtain confirmation with an independent analytical procedures within CAL, (3) prepare two lots of the same standard using independent analysis and compare, or (4) compare a new solution with a prior standard. The frequency of calibration varies, depending on instrument, but is never less frequent than once per day. After instrument calibration, one or more reference samples is checked to insure that the instrument is functioning properly. Subsequently, at a frequency of no less than one sample in ten, a reference material is checked to verify correct operation. Records of all calibrations and checks are kept in the laboratory.

Current information on the characteristics of analytical methods is provided by a continuous quality assurance program in part through a review of the quality control activities and by the "blind" insertion of split samples, spiked standards, or standard solutions into the normal sample flow. The frequency of these checks is not less than one in ten.

External performance audits for CAL are operated by the U.S. Geological Survey. In these audits, blind samples are sent to the field site operators who are instructed to pour them into the buckets and submit them as a regular sample at the end of a week during which there was no rain. Frequency of these samples is about 1 in 50. In addition to this program, CAL takes part in the interlaboratory comparison program administered and supported by the WMO and the U.S. Environmental Protection Agency. The CAL is also involved in extensive intercomparison programs with Environment Canada. Finally, an annual independent systems audit of CAL is performed by an outside expert review team.

These extensive programs insure the highest possible laboratory standards at CAL and will serve to reliably document the precision and accuracy of the data reported by the laboratory. Reports on the results of these programs are given in an annual QA report for the laboratory.

DATA MANAGEMENT

Within NADP, data management occurs in three areas; the laboratory, the Coordinator's Office, and the data bank. At the laboratory, individual datum values must be recorded properly and data for each sample verified. At the Coordinator's Office, laboratory data are combined with field reports, audit reports and site descriptions to produce a complete data file, data summaries, and other reports. At the data bank data from NADP are combined with data from other national networks, Canadian data, and data from the WMO. All data are made available to interested persons worldwide. At each step of the process, data are checked for accuracy, and to insure that the data handling steps themselves have not introduced errors into the data files.

In the laboratory, each individual datum is checked to be sure it is from a valid sample, is within the proper range, and is consistent with the history from that site. It is then combined with data for the other ionic concentrations for that sample. Then other checks, including ion balance, ratios of certain ions, and calculated versus measured pH are performed to insure that the sample is reasonable. The data are entered on magnetic tape with redundancy checks performed to insure that data entry errors are found, and sent to the Coordinator's Office.

Data evaluations are made at the Coordinator's Office with each quarterly update of the network data base. They involve both verification and validation of the data. The network data base includes descriptive and historical information about each site, chemical analysis of each sample, summaries of site operations, and audit reports. Data are checked to (1) verify that data coming from the CAL are properly indexed to the data supplied by the field observer, (2) produce an accountability of each sampling period at each site, (3) verify that all required data are in the data base, (4) evaluate all decisions made by CAL on data screening, and (5) evaluate the quality of data coming from each site.

The Acid Deposition Data System (ADS) also has a quality assurancy program to insure that no errors are introduced into the data. All computer programs are independently checked to insure that no computational mistakes are made. With each transfer of data into the system, a complete data inventory is prepared and sent to the network that produced the data to check for accuracy and completeness. In addition, each network is requested to make spot checks on specified randomly selected data values to insure that they are correct.

All of these quality assurance programs from the field site to the final data reports are done to insure the best possible data quality with known and quantified accuracy, precision, and reliability.

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REFERENCE

NADP (1984) The NADP Quality Assurance Plan issued by the National Atmospheric Deposition Program, Fort Collins, CO 80523, 40 pp.